

Stability of Transition-Metal Impurities in Ionic Fluorides from Approximate Hartree-Fock Cluster Calculations

M. BERMEJO

Departamento de Física, Facultad de Ciencias, Universidad de Oviedo, 33071 Oviedo, Spain

AND J. M. RECIO, M. FLÓREZ, VÍCTOR LUAÑA, AND L. PUEYO

Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, 33006 Oviedo, Spain

Received December 26, 1990; in revised form May 27, 1992; accepted June 1, 1992

The location of the $3d$ levels of 10 transition-metal impurities in the band gaps of four ionic fluorides has been investigated by independent Hartree-Fock (HF) cluster calculations on open-shell MF_6^{z-} systems [$M = Cr^{z+}$ ($z = 1-3$), Mn^{z+} ($z = 1-3$), Fe^{z+} ($z = 1-2$), and V^{z+} ($z = 2-3$)] and closed-shell AF_6^{z-} systems ($A = Li^+$, Na^+ , Mg^{2+} , and Zn^{2+}). The variation of the $3d$ orbital energies of the impurities with the $M-F$ distance has been deduced from the corresponding MF_6^{z-} calculations at different cluster sizes. The band gap edges for LiF, NaF, $KMgF_3$, and $KZnF_3$ have been estimated from the AF_6^{z-} calculations: the highest occupied level has been estimated from HF orbital energies of the ${}^1A_{1g}$ ground state, and the lowest unoccupied level, from HF orbital energies of the first excited ${}^3T_{1g}$ state. These orbital energies have been combined to prepare approximate energy-distance diagrams that describe the location of the $3d$ impurity levels relative to the band gap of the host crystal. The diagrams give very valuable information on the stability of the $3d$ impurity in the host and the probable lattice relaxation induced upon impurity substitution. Such information is difficult to obtain either experimentally or by means of large-scale quantum-mechanical calculations. © 1993 Academic Press, Inc.

I. Introduction

The study of transition-metal (TM) impurities in ionic crystals is a subject of continuous interest. The absorption spectra of these systems are often characterized by structures, due to the impurity ions, that appear in otherwise featureless regions of the host spectra ($I-4$). Interesting observable properties of the impurity system, like the chemical stability and the local lattice relaxations induced upon substitution, are intimately related to the location of the impurity levels

in the band structure of the host. However, the accurate determination of such locations is very difficult, either experimentally or computationally.

In this paper we present a quantum-mechanical approach to the study of the location of the $3d$ levels of a TM impurity in the band gap of an ionic crystal. The scheme is based on the use of approximate but systematic Hartree-Fock (HF) cluster calculations on a variety of TM, alkali, and alkali-earth hexafluorides. The basic idea is to find a pattern to the positions of the $3d$ levels

relative to the host band gap for a collection of systems rather than to compute the electronic structure of a particular case with a very detailed, large-scale quantum-mechanical calculation. Consideration of a variety of gradually different examples permits the identification of trends and relations among the energy of the 3d levels, the redox stability of the impurity system, and the local lattice relaxations.

To locate the 3d levels of the TM impurity in the band structure of an ionic fluoride crystal one should first compute this structure. In our approximate treatment, however, we do not proceed in this way. Instead, we limit ourselves to the determination of the edges of the band gap by means of independent cluster calculations. We estimate the top of the valence band from results of HF calculations on the ground state of a AF_6^{n-} cluster ($A = Li^+, Na^+, Mg^{2+}, Zn^{2+}$) representing the host crystal. The bottom of the conduction band is estimated from HF calculations on appropriate excited states of the same cluster. This approach may be justified when the systems considered are highly ionic and have very narrow bands. Crystals of this type have recently been described with cluster models, as documented by Lobatch *et al.* on MgO (5), Winter *et al.* on NaF (6) and NaCl (7), and Winter and Pitzer on MgF_2 (8).

The 3d levels of the impurity are deduced from HF cluster calculations on several MF_6^{n-} systems, M being the TM ion. The results of the calculations on AF_6^{n-} and MF_6^{n-} clusters are collected together in energy diagrams that show the metal–ligand dependence of the 3d levels relative to the host band gap. These energy–distance diagrams provide information on the acceptor/donor character of the 3d impurity in the host and the possible lattice relaxation induced upon impurity substitution, and are therefore useful stability diagrams.

All cluster calculations reported here have been performed with the Har-

tree–Fock–Roothaan (HFR) methodology developed by Richardson and collaborators (9) and refined in the last years by our group. This methodology has given accurate descriptions of the equilibrium geometry and $d-d$ electronic transitions of TM hexafluorides (10, 11). In Ref. (12) we reported results of cluster-*in-vacuo* calculations on LiF_6^{2-} , NaF_6^{2-} , MgF_6^{4-} , and ZnF_6^{4-} that describe well the observed geometries, band gaps, and bandwidths of LiF, NaF, $KMgF_3$, and $KZnF_3$. The good quality of these results motivated the present work.

In Section II we present our basic hypotheses and the arguments that make them, in our view, appropriate. In Section III we give numerical results. The variation of the impurity levels with the metal–ligand distance and the stability diagrams are discussed in Section IV. Our conclusions are compared with those derived from previous theoretical and semiempirical work.

II. Theoretical Basis

The band gap of an ionic crystal is associated with the energy involved in the transfer of an electron from a negative ion to a positive ion. In the ionic model, the zeroth-order band gap of a simple fluoride is thus given by the difference between the electron affinity of the fluorine atom and the appropriate ionization potential of the metal atom. As described by Cox (13), this number should be corrected by interionic overlap effects, the Madelung potential felt by the cation and the anion, and the lattice polarization.

In this work we do not consider the ionic model but the more sophisticated cluster model involving self-consistent molecular orbitals extending over a cation and its first layer of neighbor anions. In the cluster approximation, the effects of the rest of the lattice on the electronic density of the cluster must be adequately taken into account. We will see, however, that in highly ionic

compounds the cluster-*in-vacuo* stage may be adequate enough to estimate band gaps and bandwidths.

The present work is based on a series of theoretical approximations all of which have been carefully analyzed to clarify, as much as possible, the uncertainties of our results. These approximations are spelled out here in detail. The following arguments on the adequacy of our hypotheses refer to our final goal of preparing qualitative stability diagrams for *3d* impurities in fluoride crystals, as discussed in Section IV.

Our first hypothesis is that we can estimate the properties required for our study from frozen-core HFR calculations on appropriate hexafluoride clusters. As noted before, we have done these calculations with the methodology of Richardson *et al.* (9), including core-projection operators in the valence Hamiltonian and other numerical improvements described in Refs. (14–17). This hypothesis is basically justified by the quality of the results obtained by our group on a large variety of systems, as shown in Ref. (17).

The second hypothesis can be stated as follows: (i) The band-gap edges of LiF, NaF, KMgF_3 , and KZnF_3 will be computed, as in Ref. (12), from cluster calculations on the closed-shell systems LiF_6^{5-} , NaF_6^{5-} , MgF_6^{4-} , and ZnF_6^{4-} , respectively. This is supported by the quality of the results reported in Ref. (12). (ii) The *3d* levels of the TM impurities will be determined from calculations on MF_6^{z-} clusters. Again, this is based upon extensive calculations of *d-d* electronic excitations on these TM systems (17). (iii) The position of the impurity *3d* levels relative the band gap of the host will be deduced by collecting together the results of these two sets of calculations. This is a weaker assumption, only partially justified by the use of consistent computational standards in all our calculations.

The third hypothesis states that the cluster-*in-vacuo* stage will suffice to obtain

the desired qualitative picture of the *3d* levels in the band gap of the host. We have tested this idea by carefully analyzing many previous results obtained in our laboratory and by performing, for two sample species ($\text{Mn}^{2+}:\text{KZnF}_3$ and $\text{Zn}^{2+}:\text{KZnF}_3$), new cluster-in-the-lattice calculations involving the high-quality quantum lattice described in Ref. (17). This research has given us enough confidence to proceed with our analysis. In Table I we present a small sample of the extensive results supporting this approximation for the materials considered here.

The last hypothesis involves the use of the self-consistent *orbital* energies instead of *total* energies. This introduces an error due to the lack of electronic reorganization. We have computed this error in a large number of cases and in view of our results we expect the reorganization energies to be smaller than 0.6 eV in the systems analyzed here. A sample of this test is presented in Table II. The approach based on the use of orbital energies has the advantage of making the estimation of the edges of the band gap computationally consistent with the levels of the *3d* impurities estimated as orbital energies.

To compute the band gap, we first solve the HFR equations for the $^1A_{1g}$ ground state of the closed-shell AF_6^{n-} cluster. From this calculation we take the orbital energy of the highest occupied molecular orbital (MO), $\varepsilon(2p - ^1A_{1g})$. This MO is mainly a *2p* atomic orbital (AO) on the fluoride ion. Then we solve the HFR equations for the $^3T_{1u}$ state, in which the lowest unoccupied MO of the ground state is occupied with one electron. This MO is mainly an *ns* metallic AO with orbital energy $\varepsilon(ns - ^3T_{1u})$. The band gap is then approximated by the difference $\varepsilon(ns - ^3T_{1u}) - \varepsilon(2p - ^1A_{1g})$.

In the language of the ionic model, these cluster calculations involve the zeroth-order energies required for the determination of the band gap, plus the corrections due not

TABLE I
EFFECTS OF THE CLUSTER-LATTICE INTERACTION (HARTREE) ON THE BANDWIDTH OF THE VALENCE BAND FOR (A) KZnF_3 AND (B) $\text{Mn}^{2+} : \text{KZnF}_3$

A. KZnF_3	$R_{\text{ML}}(\text{bohr})$				
	3.6	3.7	3.8	3.9	4.0
VB bottom	0.37534 ^a -0.37529	0.36924 -0.38251	0.36406 -0.38904	0.35956 -0.39500	0.35558 -0.40046
VB top	0.57241 ^a -0.18391	0.54922 -0.20861	0.53031 -0.22932	0.51472 -0.24685	0.50169 -0.26179
VB bandwidth (eV)	5.36 ^a 5.21	4.90 4.73	4.52 4.35	4.22 4.03	3.98 3.77
B. $\text{Mn}^{2+} : \text{KZnF}_3$	MnF_6^{4-} in vacuo	$\text{MnF}_6^{4-} : \text{KZnF}_3$	Difference		
$\epsilon(6t_{1u}) \approx 2p_{\pi}(\text{F}^-)$	0.49055	-0.27323	-0.76378		
$\epsilon(1t_{1g}) \approx 2p_{\pi}(\text{F}^-)$	0.48314	-0.27461	-0.75775		
$\epsilon(1t_{2u}) \approx 2p_{\pi}(\text{F}^-)$	0.47403	-0.28361	-0.75764		
$\epsilon(3e_g) \approx 2p_{\sigma}(\text{F}^-)$	0.46336	-0.30931	-0.77267		
$\epsilon(1t_{2g}) \approx 2p_{\pi}(\text{F}^-)$	0.45314	-0.30400	-0.75714		
$\epsilon(5t_{1u}) \approx 2p_{\sigma}(\text{F}^-)$	0.42155	-0.33953	-0.76108		
$\epsilon(6a_{1g}) \approx 2p_{\sigma}(\text{F}^-)$	0.40113	-0.36106	-0.76219		

^a First rows: ZnF_6^{4-} in vacuo. Second rows: $\text{ZnF}_6^{4-} : \text{KZnF}_3$.

only to overlap but also to cation-anion covalency. Both corrections are automatically introduced in the self-consistent solution of the cluster equations. The coulombic, exchange, orthogonality, and polarization effects of the rest of the lattice should be in-

cluded by means of rigorous cluster-lattice interaction such as that discussed, for instance, in Ref. (17). Our third hypothesis means, however, that these lattice effects are very small for the types of interactions and systems discussed here.

TABLE II

EFFECTS OF THE REORGANIZATION ENERGY IN THE CALCULATION OF THE BAND GAP (eV)

System	R_{ML}^a	Unrelaxed ^b	Relaxed ^c	Difference
MgF_6^{4-}	3.79	17.14	16.96	0.18
NaF_6^{5-}	4.38	10.59	10.39	0.20
LiF_6^{3-}	3.80	15.14	15.42	-0.28
ZnF_6^{4-}	3.80	13.06	13.69	-0.63

^a Metal-ligand distance (bohr) used in each calculation.

^b Band gap computed as $\Delta\epsilon = \epsilon(ns - {}^3T_{1u}) - \epsilon(2p_{\text{F}} - {}^1A_{1g})$.

^c Band gap computed as $\Delta E = E({}^3T_{1u}) - E({}^1A_{1g})$.

III. Numerical Results

In Fig. 1 we depict our HFR results for the NaF_6^{5-} cluster. The mainly $3s$, $6a_{1g} - {}^3T_{1u}$ level is the first empty ns level of the cation. The highest occupied level in the ${}^1A_{1g}$ ground state is a MO dominated by a linear combination of the $2p$ fluoride orbitals. As shown in Table II, the band gap computed as a difference of orbital energies deviates by 0.2 eV from that obtained as a difference of total energies.

Our calculated band gaps, the observed values, and some results of other calculations are collected in Table III. Our values

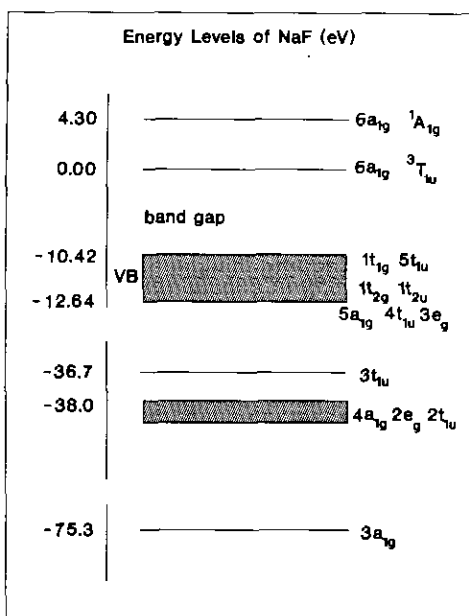


FIG. 1. Hartree-Fock energy levels for the NaF_6^{5-} cluster. The valence basis set contains $2s$, $2p$, $3s$, $3p$, and $3d$ symmetry-adapted orbitals (SAOs) centered at the Na^+ site, and $2s$ and $2p$ SAOs centered at the six fluorides.

for LiF and NaF are quite good. A discrepancy of about 4.5 eV is found for KMgF_3 . No observed value for the band gap of KZnF_3 is available, as far as we know. Our result for KZnF_3 seems to be reasonable since the ionization potential of the Zn^{2+} (18 eV) is larger than that of Mg^{2+} (15 eV), suggesting a smaller band gap for KZnF_3 . Furthermore, we recall the experimental results obtained by Beaumont *et al.* (18): the band gap of $\text{KM}F_3$ compounds ($M = \text{Mg}$, Mn , Co , and Ni) decreases when the atomic number of the M metal increases.

Our results compare well with other calculations except in the case of KMg_2F_3 . The calculations by Heaton and Lin on this system (19), like other work based on the local exchange approximation (20–22), give band gaps lower than the experimental value by several electron volts. An exchange parameter α larger than unity is required to obtain

agreement with the observed value. In local density theory, it appears that the band gap of ionic fluorides increases with the value of α and with the inclusion of the self-energy effect (20). In Hartree-Fock theory, electron correlation is expected to reduce the HFR value (23).

The impurities studied in this work are Cr^{z+} and Mn^{z+} ($z = 1-3$), Fe^{z+} ($z = 1, 2$), and V^{z+} ($z = 2, 3$). In Table IV we show,

TABLE III
EXPERIMENTALLY DETERMINED BAND GAP ENERGIES AND CALCULATED VALUES AT THE OBSERVED GEOMETRY

Material	Band gap energy (eV)		Reference
	Experimental	Calculated	
LiF		13.9	(20)
		10.6	(22)
		14.0	(23)
		14.2	(34)
		9.7	(35)
		10.9	(36)
		14.1	(37)
		14.5	(38)
		12.2	(39)
		13.6	(40)
		13.6	(41)
		14.3	(42)
		14.7	This work
		13.6	(43)
	14.2	(44)	
NaF		12.0	(21)
		9.5	(34)
		7.7	(35)
		12.7	(38)
		10.6	This work
		11.5	(43)
	11.7	(45)	
KMgF_3		7.2 ^a	(19)
		12.4 ^b	(19)
		16.6	This work
		11.8	(18)
	12.4	(46)	
KZnF_3		12.8	This work

^a Computed with $\alpha = 1$.

^b Computed with $\alpha = 1.2$.

TABLE IV
STABILIZATION OF THE ENERGY LEVELS (eV) OF THE MnF_6^{4-} CLUSTER ($R = 4.0$ bohr) PRODUCED BY THE LATTICE POTENTIAL OF THE KZnF_3 (LATTICE SIZE 3.83 bohr)

MO	AO ^b	Lattice model ^a		
		Point charge	Coulomb	Coulomb + Exch.
$\epsilon(\text{Mn}^{2+}; \text{KZnF}_3) - \epsilon(\text{cluster-in-vacuo})$				
$6a_{1g}$	$2p_{\sigma}(\text{F}^-)$	-21.28	-20.79	-20.73
$6t_{1u}$	$2p_{\pi}(\text{F}^-)$	-20.98	-20.82	-20.79
$4e_g$	$3d_{\sigma}(\text{Mn}^{2+})$	-20.95	-21.09	-21.12
$2t_{2g}$	$3d_{\pi}(\text{Mn}^{2+})$	-20.94	-21.09	-21.11

^a Reference (17).

^b Largest component of the MO.

as an example, the stabilization gained by some relevant orbital energies of the MnF_6^{4-} cluster when the cluster–lattice interaction is included. We see that simple point-charge lattice models and detailed quantum lattice models, including Coulomb and exchange interactions (17), give, within tenths of an electron volt, the same stabilization for the 3d levels.

To show the cluster effects on the free-ion levels of the TM impurities, we collect in Table V the 3d orbital energies for the

species studied here. A negative constant has been added to all cluster energies to facilitate the comparison. We observe that the cluster effect increases with the cationic charge, revealing the increasing action of cluster covalency. These numbers are discussed further in the next section.

The possibility of studying the variation of the 3d orbital energy with the metal–fluoride distance R is an important result of the cluster analysis. According to our calculations, these energies are decreasing functions of R with similar slopes for all ions considered here. Figure 2 depicts the R dependence of the highest occupied 3d MO of the TM impurities. A vertical tick in each curve indicates the theoretical equilibrium distance $R_e(M-F)$ obtained in the corresponding cluster-*in-vacuo* calculation. The band gap edges have been obtained, as indicated, from the corresponding AF_6^{z-} calculation at $R_e(A-F)$ (12). They are marked in this figure by solid horizontal lines. The theoretical equilibrium distance of the host lattice is indicated as a vertical dotted line.

As is well known (2, 24–28), some relaxation of the fluoride ions should be expected upon impurity substitution. This effect can be qualitatively discussed with the help of the diagrams in Fig. 2. They can be used

TABLE V
FREE-ION AND CLUSTER-*in-Vacuo* 3d ORBITAL ENERGIES (eV) COMPUTED AT $R(M-F) = 4.0$ bohr

Ion	$\epsilon_{3d}(\text{free ion})^a$	$\epsilon_{3d}(\text{cluster})$	Difference
$\text{Cr}^+(d^5)$	-17.67	-17.66	-0.01
$\text{Mn}^+(d^6)$	-18.16	-18.07	-0.09
$\text{Fe}^+(d^7)$	-19.40	-20.38	0.98
$\text{V}^{2+}(d^3)$	-30.35	-30.58	0.23
$\text{Cr}^{2+}(d^4)$	-32.56	-30.04	-2.52
$\text{Mn}^{2+}(d^5)$	-35.05	-34.53	-0.52
$\text{Fe}^{2+}(d^6)$	-35.83	-36.30	0.47
$\text{V}^{3+}(d^2)$	-47.30	-42.83	-4.47
$\text{Cr}^{3+}(d^3)$	-50.41	-45.69	-4.72
$\text{Mn}^{3+}(d^4)$	-53.22	-44.60	-8.62

^a From Reference (47).

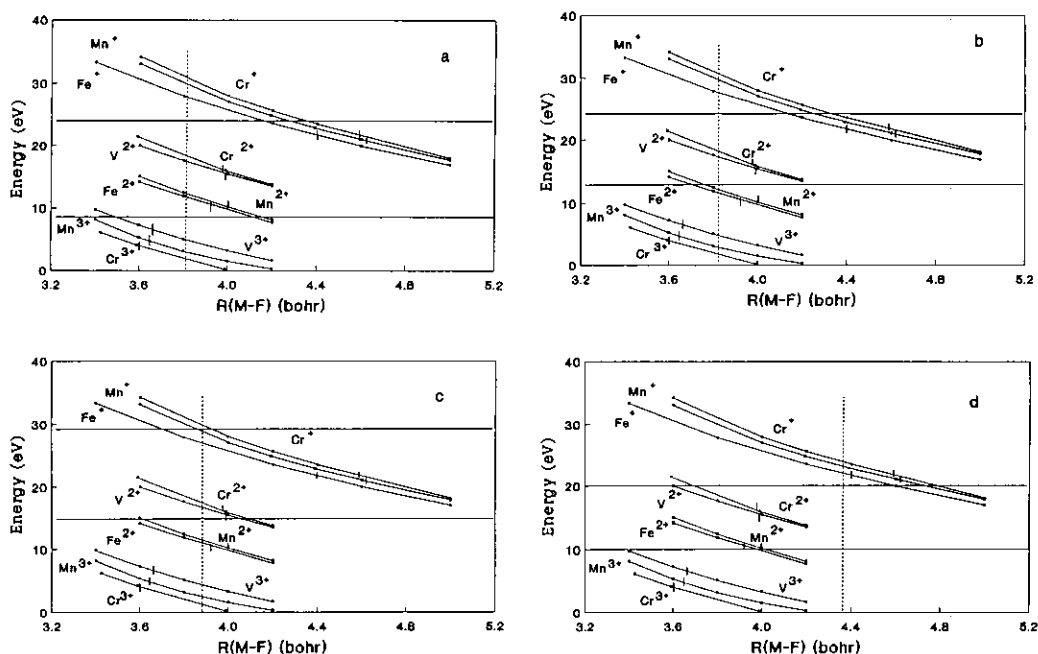


FIG. 2. Variation of the 3d orbital energies of transition-metal impurities with the metal-ligand distance in (a) KMgF_3 , (b) KZnF_3 , (c) LiF , and (d) NaF . Solid horizontal lines delimit the computed band gap. Dashes in the energy curves indicate the theoretical $R_c(M-F)$ distance. The vertical dotted line corresponds to the theoretical R_c of the host.

in two ways. If the local geometry of the impurity is known, the positions of the impurity levels within the band gap can be obtained. Alternatively, if we know the location of the 3d levels relative to the band gap, we can predict the relaxation of the nearest-neighbor ions.

IV. Stability Criteria, Redox Processes, and Local Relaxation

Using the results of our calculations and the empirical analysis reported by Agulló-López *et al.* (29, 30), we now discuss stability criteria that may be useful in understanding the general behavior of TM impurities in ionic fluorides.

The energy range including the host band gap can be divided into three regions related to the stability of the substitutional impuri-

ties. The bottom part of the conduction band is an unstable region for an open-shell TM impurity. Impurities with their 3d levels in this part can give electrons to this empty band, acting as reducing impurities or hole traps. The top part of the valence band is also an unstable region. Electrons from this filled band can reach the partially occupied 3d level of a TM impurity. Cations with their 3d levels in this region can act as electron traps. Finally, if the impurity has its partially occupied 3d levels within the band gap, it is most likely to be stable.

According to these stability criteria, 3d ions can clearly modify their redox character when R changes. To see this, let us consider the energy of the 3d levels in Fig. 2 at the value of R corresponding to the unrelaxed host lattice, i.e., at the vertical dotted line.

TABLE VI
 CATIONS ORDERED BY DECREASING VALUE OF THE CATION-FLUORIDE DISTANCE

Lattice	Impurity-fluoride relative distance
LiF	$Cr^+ \approx Mn^+ > Fe^+ > Cr^{2+} \approx V^{2+} > Li^+ > Mn^{2+} \approx Fe^{2+} > V^{3+} > Mn^{3+} > Cr^{3+}$
NaF	$Cr^+ > Mn^+ > Fe^+ > Na^+ > Cr^{2+} \approx V^{2+} \approx Mn^{2+} \approx Fe^{2+} > V^{3+} > Mn^{3+} > Cr^{3+}$
KMgF ₃	$Cr^+ > Mn^+ > Fe^+ > Cr^{2+} \approx V^{2+} \approx Mn^{2+} > Fe^{2+} > Mg^{2+} > V^{3+} > Mn^{3+} > Cr^{3+}$
KZnF ₃	$Cr^+ > Mn^+ > Fe^+ > Cr^{2+} \approx V^{2+} > Zn^{2+} > Mn^{2+} > Fe^{2+} > V^{3+} > Mn^{3+} > Cr^{3+}$
Cluster-in-vacuo	$Mn^+ \approx Cr^+ > Fe^+ > Na^+ > Mn^{2+} \approx V^{2+} \approx Cr^{2+} \approx Fe^{2+} > Li^+ > Mg^{2+} \approx Zn^{2+} > V^{3+} \approx Mn^{3+} \approx Cr^{3+}$

Note. Each line refers to a series of cation impurities in the host listed on the left.

We see that the monovalent cations have their 3d levels above the bottoms of the conduction bands in NaF, KMgF₃, and KZnF₃. Thus, they would be unstable in these crystals. An outward shift of their nearest neighbors would be represented in

 TABLE VII
 OBSERVED AND CALCULATED EQUILIBRIUM METAL-FLUORIDE DISTANCES (Å) FOR 3d IONS IN LiF, NaF, KMgF₃, AND KZnF₃

	LiF	NaF	KMgF ₃	KZnF ₃	Cluster-in-vacuo
R_0	2.05	2.31	2.02	2.02	—
	2.01	2.31	1.99	2.03	
Cr ⁺	—	2.47 ^a	2.34 ^a	—	2.42 ^b
Mn ⁺	—	—	—	—	2.43 ^b
Fe ⁺	2.22 ^c	2.35 ^c	2.23 ^c	—	2.32 ^b
V ²⁺	2.01 ^d	—	2.05 ^b	—	2.11 ^b
Cr ²⁺	—	—	2.05 ^b	—	2.10 ^b
Mn ²⁺	≪2.07 ^e	2.15 ^f	2.06 ^g	2.06 ^g	2.12 ^b
			2.07 ^f	2.09 ^f	
			2.07 ^b	2.01 ^h	
				2.08 ⁱ	
Fe ²⁺	—	—	—	—	2.07 ^b
V ³⁺	—	—	1.92 ^b	—	1.94 ^b
Cr ³⁺	—	—	1.89 ^b	—	1.91 ^b
Mn ³⁺	—	—	1.91 ^b	—	1.93 ^b

^a Reference (31).

^b Reference (10).

^c Reference (32).

^d Reference (26).

^e Reference (33).

^f Reference (25).

^g Reference (48).

^h Reference (17).

ⁱ Reference (49).

this figure by a shift of the dotted line to the right. This would take the 3d levels within the band gap and would stabilize these TM impurities. In the LiF lattice, the Mn⁺ and Fe⁺ ions have their 3d levels within the band gap. These ions should thus be stable in LiF. This would also be the case for Cr²⁺ and V²⁺ in the four lattices considered here. The Mn²⁺ and Fe²⁺ ions show stability only in KMgF₃. Their 3d levels appear below the tops of the valence bands in KZnF₃, LiF, and NaF. Without first-neighbors relaxation those ions would act as electron traps. An inward relaxation of the first fluoride shell would put their 3d levels within the band gap. This R shift should be larger in NaF and LiF than in KZnF₃. Finally, the tripositive ions have their 3d levels well below the tops of the valence bands in the four crystals. These impurities would be reducing species. Only a quite large decrease in R would make them stable in these lattices.

In summary, the higher (lower) the position of the 3d levels relative to the bottom (top) of the conduction (valence) band, the larger the outward (inward) first-neighbor relaxation should be to make the oxidation state stable in the host. Impurities having 3d levels within the band gap would not require lattice relaxation to become stable.

The above discussion suggests an ordering of the TM impurities in different hosts. In Table VI the TM cations are listed in

order of decreasing impurity–ligand equilibrium distance for a given lattice. To prepare this qualitative table we had to assign a most probable equilibrium distance to every TM ion–host pair. In doing so, we used the following criteria: (i) TM ions having their $3d$ levels within the band gap for $R = R_e(\text{host})$ are expected to be stable. Their assigned distance is, as a first-order approximation, the cluster-*in-vacuo* value noted by a tick in Fig. 2. (ii) TM ions with $\epsilon[R = R_e(\text{host})]$ in the conduction band are expected to be unstable. They would be stabilized by an outward shift of the fluorides. Their assigned equilibrium distances are given by the crossing of their $\epsilon(R)$ line with the bottom of the conduction band. (iii) TM ions having $\epsilon[R = R_e(\text{host})]$ in the valence band are unstable and could be stabilized by an inward shift. Their assigned equilibrium distance is given by the crossing of their $\epsilon(R)$ curve with the top of the valence band.

We present in Table VII a compilation of experimental and theoretical values of R_e for the impurity systems studied here. We see that the ordering of the $3d$ ions in KMgF_3 is in complete agreement with the corresponding series in Table VI. We also see that the inward relaxation of the tripositive ions and the outward relaxation of the monovalent and divalent ions are correctly predicted by the diagrams in Fig. 2. Furthermore, the shifts observed in going from cluster-*in-vacuo* to cluster-in-the-lattice calculations (Table VII) are also consistent with our stability diagrams. For instance, an inward shift can be expected in passing from *vacuo* to the lattice for $\text{Cr}^{2+} : \text{KMgF}_3$ (Fig. 2a) since its $R_e(\text{in vacuo})$ is larger than $R_e(\text{host})$. An outward relaxation for $\text{Mn}^{2+} : \text{NaF}$ (Fig. 2d) can be expected for equivalent reasons. The distances in Table VII confirm this.

V. Concluding Remarks

For the $3d$ ions and the ionic fluoride crystals studied in this work by means of HF

cluster models, the almost constant stabilization of the cluster $3d$ levels produced by the cluster–lattice interaction reveals that the cluster-*in-vacuo* approximation may be accurate enough to give the positions of the TM impurity levels relative to the host band gap.

The analysis of the stability diagrams deduced from results of HF calculations shows that the position of the impurity levels within the band structure of the host is intimately related to its local equilibrium geometry. The cluster-*in-vacuo* approach reveals how the electronic behavior of the TM impurity changes with the metal–ligand distance.

The analysis of the orbital energies of TM impurities presented in this work gives information in good agreement with experimental results and other accurate and expensive theoretical calculations.

Acknowledgments

We thank E. Francisco and A. Martín Pendás for long and stimulating discussions. We are also grateful to the Vicerrectorado de Investigación, Universidad de Oviedo, for the CONVEX-VAX facility. Financial support from the Dirección General de Investigación Científica y Tecnológica, Project PB86-0240, is gratefully acknowledged.

References

1. J. F. SABATINI, A. E. SALWIN, AND D. S. McCLURE, *Phys. Rev. B* **11**, 3832 (1975).
2. D. B. CHASE AND D. S. McCLURE, *J. Chem. Phys.* **64**, 74 (1976).
3. J. SIMONETTI AND D. S. McCLURE, *Phys. Rev. B* **16**, 3887 (1977).
4. R. A. SHATWELL AND D. S. McCLURE, *J. Chem. Phys.* **70**, 2081 (1979).
5. V. A. LOBATCH, A. B. SOBOLEV, I. R. RUBIK, O. E. TAURIAN, AND J. L. CALAIS, *Int. Quantum Chem. Symp.* **18**, 121 (1984).
6. N. W. WINTER, R. M. PITZER, AND D. K. TEMPLE, *J. Chem. Phys.* **86**, 3549 (1987).
7. N. W. WINTER, R. M. PITZER, AND D. K. TEMPLE, *J. Chem. Phys.* **87**, 2945 (1987).
8. N. W. WINTER AND R. M. PITZER, *J. Chem. Phys.* **89**, 446 (1988).
9. J. W. RICHARDSON, T. F. SOULES, D. M. VAUGHT, AND R. R. POWELL, *Phys. Rev. B* **4**, 1721 (1971).

10. V. LUAÑA, G. FERNÁNDEZ RODRIGO, M. FLÓREZ, E. FRANCISCO, J. M. RECIO, J. F. VAN DER MAELEN, L. PUEYO, AND M. BERMEJO, *Cryst. Latt. Def. Amorph. Mater.* **15**, 19 (1987).
11. E. FRANCISCO, M. FLÓREZ, Z. BARANDIARÁN, G. FERNÁNDEZ RODRIGO, V. LUAÑA, J. M. RECIO, M. BERMEJO, L. SEJO, AND L. PUEYO, *Cryst. Latt. Def. Amorph. Mater.* **15**, 45 (1987).
12. M. BERMEJO, V. LUAÑA, J. M. RECIO, AND L. PUEYO, *J. Mol. Struct. (Theochem)* **166**, 235 (1988).
13. P. A. COX, "The Electronic Structure and Chemistry of Solids", Chap. 3, Oxford Univ. Press, New York (1987).
14. L. SEJO, Z. BARANDIARÁN, V. LUAÑA, AND L. PUEYO, *J. Solid State Chem.* **61**, 269 (1986).
15. V. LUAÑA, Ph.D. thesis, Universidad de Oviedo (1987).
16. E. FRANCISCO, Ph.D. thesis, Universidad de Oviedo (1988).
17. V. LUAÑA, M. BERMEJO, M. FLÓREZ, J. M. RECIO, AND L. PUEYO, *J. Chem. Phys.* **90**, 6409 (1989).
18. J. H. BEAUMONT, A. J. BOURDILLON, AND J. BORDAS, *J. Phys. C: Solid State Phys.* **10**, 333 (1977).
19. R. A. HEATON AND C. C. LIN, *Phys. Rev. B* **25**, 3538 (1982).
20. A. ZUNGER AND A. J. FREEMAN, *Phys. Rev. B* **16**, 2901 (1977).
21. N. E. BRENER AND J. L. FRY, *Phys. Rev. B* **6**, 4016 (1972).
22. W. P. MENZEL, C. C. LIN, D. F. FOUQUET, E. E. LAFON, AND R. C. CHANEY, *Phys. Rev. Lett.* **30**, 1313 (1973).
23. A. B. KUNZ, *Phys. Rev. B* **26**, 2056 (1982).
24. T. P. P. HALL, W. HAYES, R. W. H. STEVENSON, AND J. WILKENS, *J. Chem. Phys.* **38**, 1977 (1963).
25. M. T. BARRIUSO AND M. MORENO, *Phys. Rev. B* **29**, 3623 (1984).
26. R. A. HEATON AND C. C. LIN, *J. Phys. C: Solid State Phys.* **18**, 3211 (1985).
27. A. B. KUNZ, *Phys. Rev. B* **38**, 1064 (1988).
28. J. A. ARAMBURU, M. MORENO, AND M. T. BARRIUSO, *Cryst. Latt. Def. Amorph. Mater.* **16**, 215 (1987).
29. F. AGULLÓ-LÓPEZ AND F. J. LÓPEZ, *Cryst. Latt. Def. Amorph. Mater.* **9**, 131 (1981).
30. F. AGULLÓ-LÓPEZ, F. J. LÓPEZ, AND F. JAQUE, *Cryst. Latt. Def. Amorph. Mater.* **9**, 227 (1982).
31. G. FERNÁNDEZ RODRIGO, L. PUEYO, M. MORENO, AND M. T. BARRIUSO, *J. Solid State Chem.* **67**, 64 (1987).
32. G. FERNÁNDEZ RODRIGO AND L. PUEYO, *J. Chim. Phys.* **84**, 821 (1987).
33. M. MORENO, F. RODRÍGUEZ, J. A. ARAMBURU, F. JAQUE, AND F. J. LÓPEZ, *Phys. Rev. B* **28**, 6100 (1983).
34. M. MATOS AND B. MAFFEO, *Solid State Commun.* **48**, 961 (1983).
35. S. ANTOCI AND L. MIHICH, *Phys. Rev. B* **21**, 799 (1980).
36. R. C. CHANEY, E. E. LAFON, AND C. C. LIN, *Phys. Rev. B* **4**, 2734 (1971).
37. D. J. MICKISH, A. B. KUNZ, AND T. C. COLLINS, *Phys. Rev. B* **9**, 4461 (1974).
38. F. PERROT, *Phys. Status Solidi* **52**, 163 (1972).
39. M. R. HAYNS, *J. Phys. C* **5**, 15 (1972).
40. L. J. PAGE AND E. H. HYGH, *Phys. Rev. B* **1**, 3472 (1970).
41. N. E. BRENER, *Phys. Rev. B* **7**, 1721 (1973).
42. G. S. PAINTER, *Int. J. Quantum Chem. Symp.* **5**, 501 (1971).
43. D. M. ROESSLER AND W. C. WALKER, *J. Phys. Chem. Solids* **28**, 1507 (1967).
44. M. PIACENTINI, *Solid State Commun.* **17**, 697 (1975).
45. S. NAKAI AND T. SAGAWA, *J. Phys. Soc. Japan* **26**, 1427 (1969).
46. H. TAKAHASHI AND R. ONAKA, *J. Phys. Soc. Japan* **43**, 2021 (1977).
47. E. CLEMENTI AND C. ROETTI, *At. Data Nucl. Tables* **14**, 177 (1974).
48. J. RUBIO, H. MURRIETA, AND G. AGUILAR, *J. Chem. Phys.* **71**, 4112 (1979).
49. A. LEBLÉ, Thèse d'Etat, Université du Maine (1982).